

# SUPPLEMENTARY INFORMATION

## **Synthetically chemical-electrical mechanism for controlling large scale reversible deformation of liquid metal objects**

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## SI Appendix 1: Mechanism of the reversible deformation with the equivalent circuit

### 1. Before application of the external voltage

Generally, the liquid gallium would form into a spheroid in the aqueous solution through injection due to its extremely high surface tension, and the hydrostatic pressure resulted from gravity slightly distorts the shape of the droplet, as illustrated in **Fig. S1-A**. In the NaOH solution, gallium can react with the alkali solution slowly, producing gallates like  $[\text{Ga}(\text{OH})_4]^-$ , which make the surface of gallium negatively charged and cations accumulate nearby<sup>1</sup>. These anions induce the formation of a diffuse electrical double layer (EDL) across the liquid gallium and the solution. Therefore, the equivalent circuit includes the electrolyte resistance as well as the resistance and capacitance of the EDL, respectively (**Fig. S1-A**).

### 2. During application of the external voltage

Theoretically, the change of the surface tension between the liquid metal and the electrolyte directly induced by the external electricity can be described by Lippmann's equation when the voltage is not sufficient to produce electrolytic reaction, i.e.

$$\gamma = \gamma_0 - \frac{1}{2} c V^2 \quad (1)$$

where,  $\gamma$  is the surface tension,  $c$  is the capacitance of electric double layer per unit area,  $V$  is the potential difference across the electrical double layer (EDL),  $\gamma_0$  is the maximum surface tension when  $V = 0$ .

Clearly, the introduction of the external power supply reduces the initial surface tension of the liquid metal slightly. Following the Young–Laplace equation, the pressure difference  $p$  across the electrolyte and the liquid metal droplet can be given as follows:

$$p = \gamma \cdot \frac{2}{r} \quad (2)$$

where,  $1/r$  is the curvature of the droplet surface.

Additionally, redox reaction between the two electrodes proceeds when the voltage is above a critical value. The oxidation reaction on the anode is divided into two parts: oxygen is electrochemically formed on the platinum electrode, of which part contacts with the electrolyte solution, while a thin layer of gallium oxide is produced on the surface of the liquid metal gallium. The mass of the products on the anode, including oxygen and the oxide gallium, can be calculated according to the Faraday's law of electrolysis, i.e.

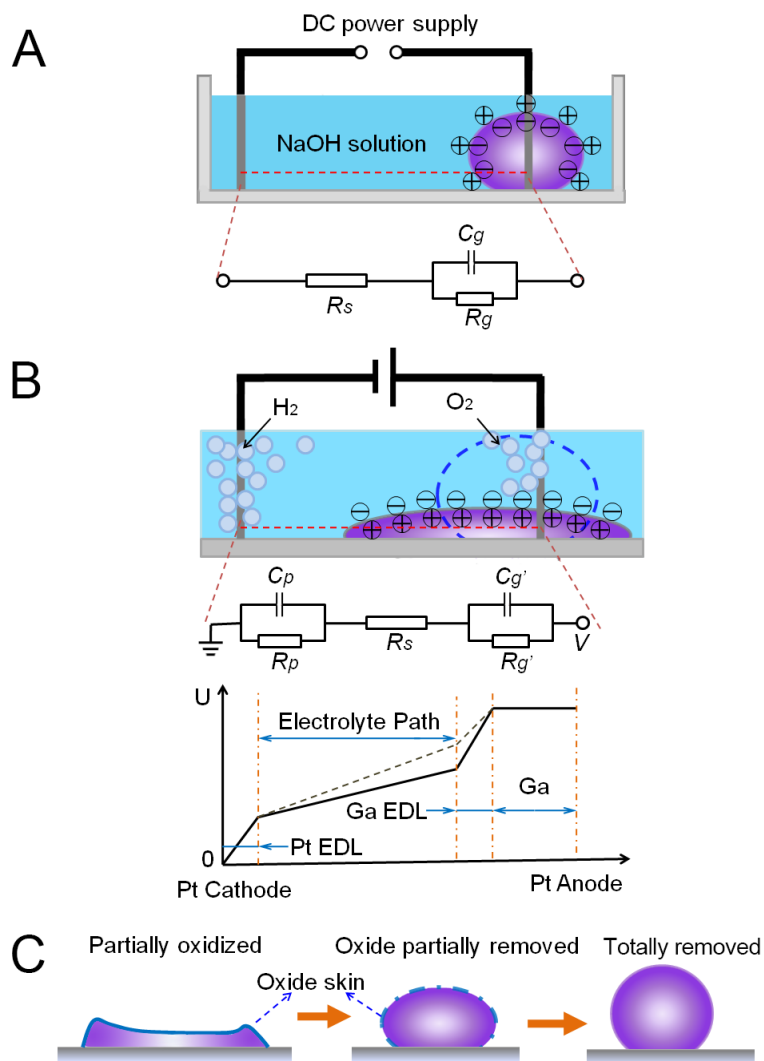
$$m = kIt \quad (3)$$

$$k = \frac{Mq}{Fn} \quad (4)$$

where,  $m$  is the mass of the products on the anode,  $I$  and  $t$  are the intensity of the electric current and power-on time, respectively,  $k$  is the electrochemical equivalent,  $M$  is the molar mass of the products on the anode,  $n$  is the valency of the products, and  $F=9.65 \times 10^4$  C/mol is the Faraday's constant. The amount of the oxide layer still depends on the intensity of the electric current and the power-on time.

The surface tension of a liquid results from the imbalanced molecular attraction from two sides of the interface across a liquid and an immiscible fluid.<sup>2</sup> The formation of the solid oxide skin disturbs the fluidity and hinders the contact between the two original fluids. Therefore, the surface tension is decreased with the formation of the solid oxide layer, which induces the droplet into a pronounced nonspherical shape.<sup>2</sup> As the drop of electric current across the EDL is less on the side toward the cathode, the formation of the oxide gallium is faster on this side, and thus the deformation near the cathode is prior to that far away from the cathode. That is to say, the electric current near the cathode is larger than that away from the cathode due to larger resistance with longer current path, which directly results in that the oxide skin is thicker on the metal surface near the cathode. Thus, the surface tension drop is larger near the cathode, and consequently, according to Eq. (2), the pressure difference away from the cathode is larger than that near the cathode, which pushes the metal to deform toward the cathode. Eventually, the deformation is asymmetric and tends to moving toward the cathode, as shown in **Fig. S1-B**. The surface tension of the liquid metal gallium is about 700mN/m, which is larger than other liquid metal alloys.<sup>3</sup> Once the surface tension of the liquid gallium decreases, the hydrostatic pressure due to gravity will lower the center of gravity, which leads to the further deformation. However, the continuous accumulation of the oxide gallium hampers the deformation when the oxide layer is thick enough as the solid oxide skin reduces the fluidity of the liquid gallium.

The introduction of the external voltage updates the equivalent circuit, including the addition of the EDL across the platinum cathode and the solution, the changed EDL across the gallium droplet and the solution. The change of the EDL across the gallium droplet and the solution is not only induced by the conversion of the anions, but also the formation of the oxide skin. Since the metal gallium owns very high conductivity, it can be regarded as part of the anode, and thus the gallium droplet is equipotential. **Fig. S1-B** displays the new equivalent circuit, where the dashed line refers to the state under longer electrolyte path. As depicted in this figure, the electrolyte path affects the EDL of gallium as well.



**Supplementary Figure S1 | The schematic of working mechanism for the reversible deformation and the related equivalent circuit.** (A) Schematic of the experimental setup and the equivalent circuit without external power supply:  $R_s$  is the electrolyte resistance between the two electrodes;  $R_g$  and  $C_g$  are the double-layer capacitance and the charge-transfer resistance of the EDL between the gallium droplet and the solution, respectively. (B) Schematic of the gallium droplet surface charge redistribution and the equivalent circuit when the direct power is applied:  $R_s$  is the electrolyte resistance between the two electrodes;  $R_p$  and  $C_p$  are the double-layer capacitance and the charge-transfer resistance of the EDL between the platinum electrode and the solution due to addition of the external voltage, respectively;  $R_g'$  and  $C_g'$  are the changed double-layer capacitance and the charge-transfer resistance of the EDL between the gallium droplet and the solution, respectively. (C) Schematic of the gallium morphology after removing the external power: the deformed liquid droplet with the coating of oxide gallium reversibly and gradually reconfigures itself into a sphere along with the dissolution of the oxide skin.

When the electrolyte solution is acidic or alkaline, the oxide gallium can be dissolved. In the NaOH solution, the concentration and the temperature of the solution determine the rate of the dissolution. The dissolution facilitates the deformation in some degree as the oxide layer hinders the deformation, which is confirmed by substituting the Na<sub>2</sub>SO<sub>4</sub> solution for the NaOH solution. Thus, the reversibility immensely depends on the chemical dissolution of the oxide layer.

### 3. After removing the external voltage

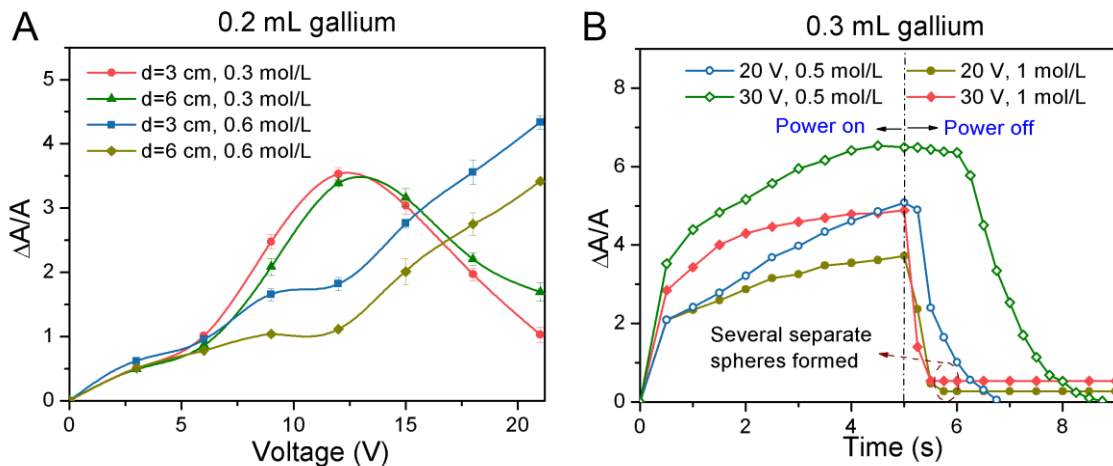
In the neutral solution, no obvious shape variational phenomenon is observed. However, in the acidic or alkaline solution which can dissolve the oxide gallium, the deformed gallium is reversibly contracted back again into a sphere along with the dissolution. The gradual reconfiguration can be exhibited in **Fig. S1-C**.

## **SI Appendix 2: Effect of the voltage on the reversible deformation in the NaOH solution while other conditions are fixed.**

Upon a direct voltage, the electric current increases along with increase of the voltage. When the voltage is low, the rate of the oxide gallium formation becomes slow, which results in that the oxide gallium is dissolved immediately, and thus no obvious deformation takes place. When the voltage is appropriate, the rate of oxidation becomes slightly faster than that of the dissolution, and the deformation proceeds, as shown in **Fig. S2-A**. When the voltage is above a certain value, the generation rate of the oxide gallium is so fast that the oxide gallium quickly coats on the surface of the gallium, which conversely hinders the deformation. In general, the voltage controls the rate of the oxide gallium formation, and the rate difference between the formation and the dissolution determines the residual oxide layer, which consists of the essential factor to affect the deformation (**Fig. S2-B**). If the rate difference is negative or approximates to zero, no deformation can be observed. If the rate difference is positive and not too much different, the deformation takes place and the performance of the deformation relies on the rate difference. If the rate difference is quite large, evident oxide gallium is accumulated and continuously thickened, while the deformation is very restricted. Additionally, the rate difference affects the time to dissolve the oxide layer as well. The more the oxide gallium accumulates, the longer time it takes.

With the application of dynamic voltage (above zero), such as voltage with sine wave, the performance of the deformation is dynamically changed along with the voltage. In contrast to the square-wave voltage, the rate of extension and contraction are both slowed down as the voltage

changes along with the time.

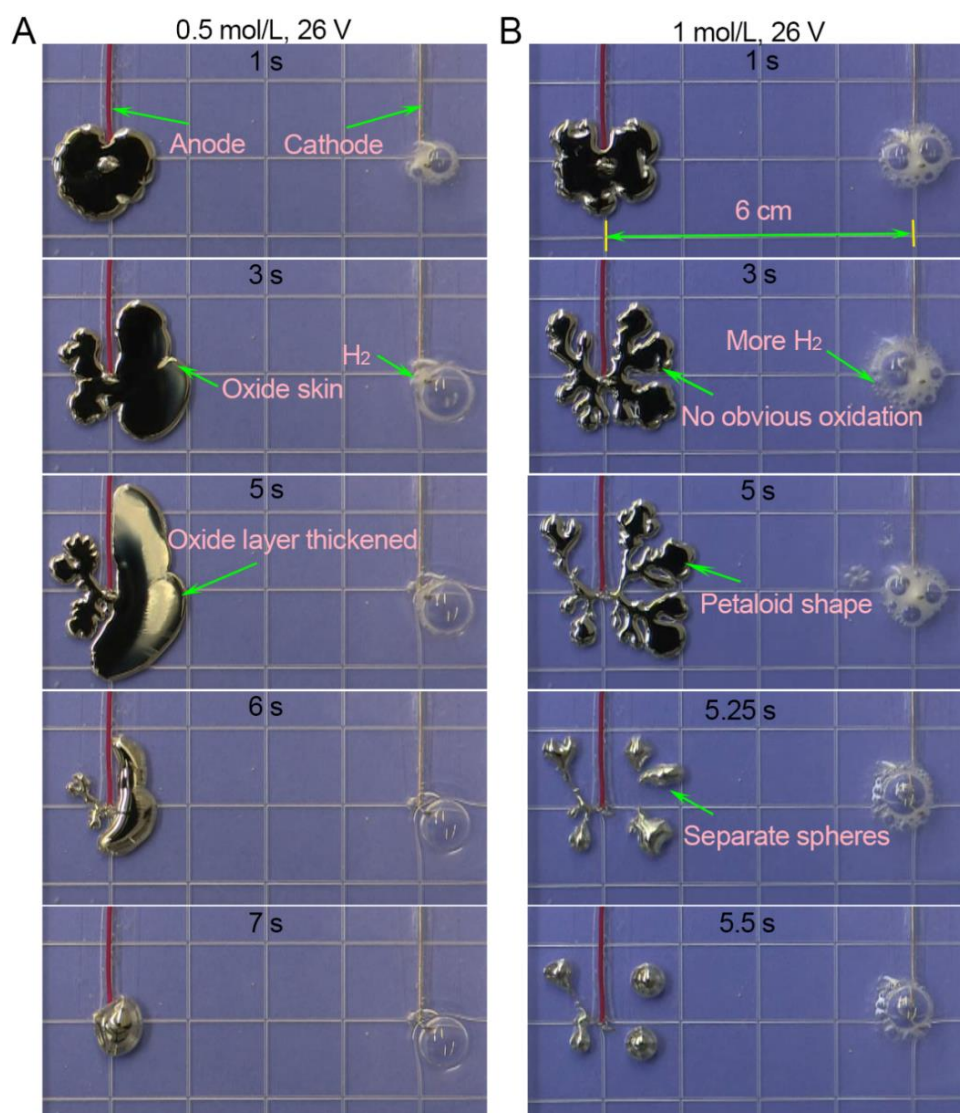


**Supplementary Figure S2** | The deformability among different voltages and between two typical concentrations of NaOH solution. The vertical coordinate of (A) and (B) both refer to the relative change of cross sectional area, where the symbol  $\Delta A$  and  $A$  denote the change of the cross sectional area and the original cross sectional area, respectively. The power-on time lasts for five seconds. (A) The relative change of cross sectional area at the fifth second under different voltages and NaOH solution concentrations. (B) The relative change of cross sectional area along with the time under different voltages and NaOH solution concentrations.

### SI Appendix 3: Effect of the solution concentration on the reversible deformation in the NaOH solution while other conditions are fixed.

The concentration of the NaOH solution affects the intensity of the electric current, which is closely related to the formation of the oxide gallium, as calculated by Eq. (3). On the other side, the concentration of the NaOH solution determines the rate of the oxide layer dissolution. The two roles are opposite, and thus it is not easy to control the deformation via the solution concentration accurately. However, the concentration of the NaOH solution is very important to the rate of both extension and contraction. As shown in **Fig. S2-B**, under the condition of high external voltage and high concentration of NaOH solution, both the formation and the dissolution are so fast that the accumulation of the oxide gallium appears less accordingly. As a result, the surface tension drops a little slower, and the gallium reversibly contracts faster. Meanwhile, along with the fast dissolution, the oxide gallium is not sufficient enough to hinder the deformation, and thus under high voltages, the deformability is improved, as shown in **Fig. S2-A**. In the high concentration of NaOH solution, once the voltage is removed, the gallium reconfigures itself immediately due to

the not much accumulation and fast dissolution (**Fig. S2-B**). Additionally, since the gallium deforms into a petaloid shape, the over quick deformation can lead to the rupture of the petals. In addition, several separate smaller spheres can be formed when the rate of the contraction becomes too fast as the gallium petals near the center of the flower becomes much thinner, as shown in **Fig. S2-B**.



**Supplementary Figure S3 | Sequential snapshots for reversible deformation of liquid metal upon two typical concentrations of NaOH solution.** The applied voltage and electrode spacing are 26 V and 6 cm, respectively. (A) The concentration of the NaOH solution is 0.5 mol/L. (B) The concentration of the NaOH solution is 1 mol/L.

**Fig. S3** shows the reversible deformation of the liquid gallium under different concentrations of NaOH solution. In contrast to the experiment operated in the 0.5 mol/L NaOH solution (**Fig.**

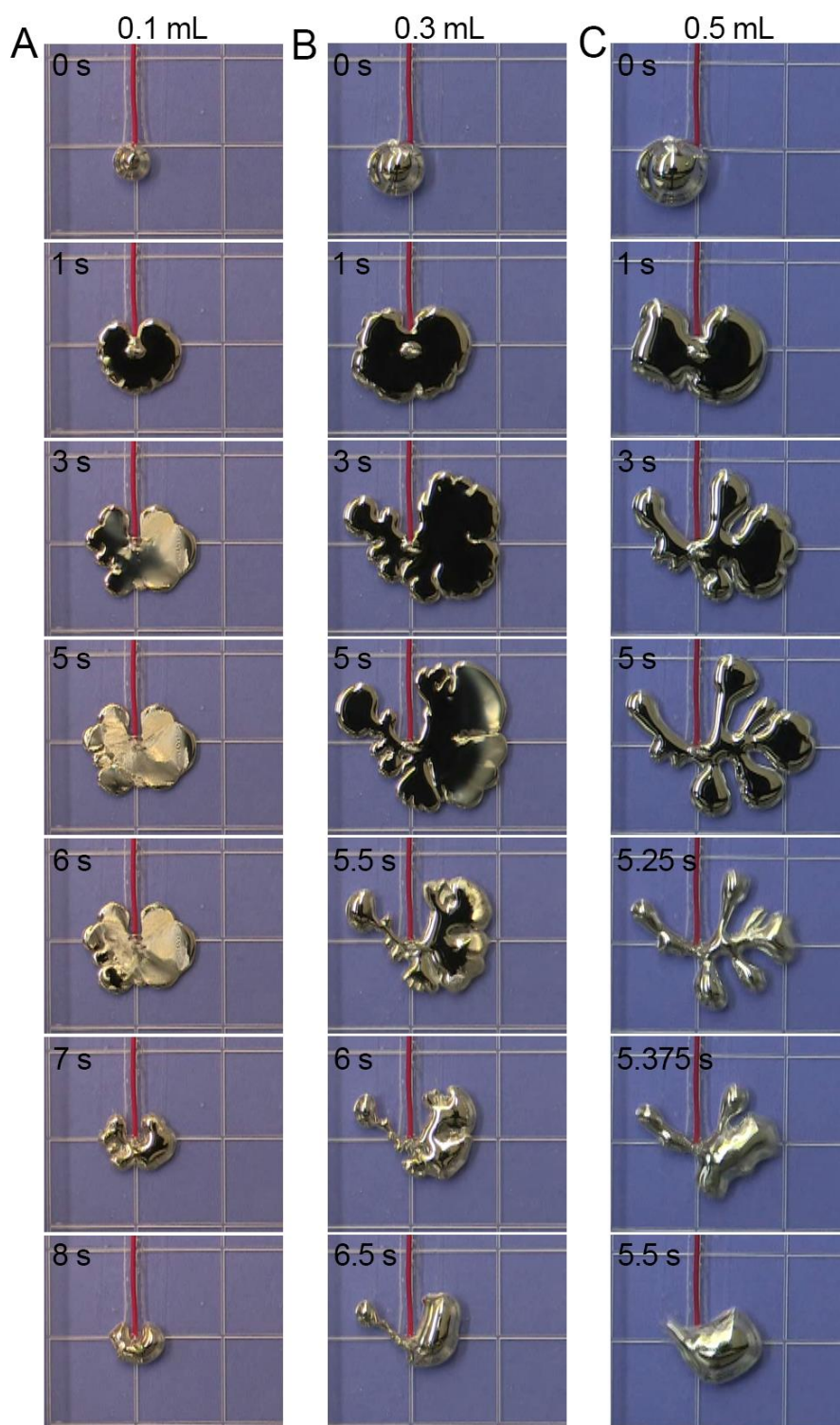
**S3-A**), regarding the 1 mol/L NaOH solution, the production of the hydrogen appears much more since the higher concentration reduces the electrical resistance along the current path and thus increases the electrical current, as calculated in Eq. (3). Theoretically, the larger electrical current also facilitates the generation of the oxide skin. However, no obvious oxide layer is observed as the higher concentration of NaOH solution also accelerates the oxide dissolution. In addition, the final reconfiguration is the formation of several smaller separate spheres rather than a single one. The main reason for the different reconfigurations is that in the higher concentration of NaOH solution, more petals are likely to be formed, as displayed in **Fig. S3-B**.

#### **SI Appendix 4: Effect of the liquid gallium volume on its reversible deformation in the NaOH solution while other conditions are fixed.**

At the beginning of applying the voltage, when ignoring the influence of the gallium volume on the electric field, the stronger initial surface tension by the larger gallium volume can accelerate the dissolution of the oxide layer since the oxide skin covers a larger surface, which makes the oxide layer thinner. When the concentration of the applied NaOH solution becomes appropriate, the deformability of different sized gallium droplets varies from voltage to voltage. Under the exposure of high external voltage, it is favorable for a larger droplet to deform as the rate difference between the formation and dissolution is relatively reduced. On the contrary, under the low external voltage, the deformability of smaller gallium droplet becomes better since the rate of the oxide gallium formation is slow. Therefore, in order to improve the performance of the deformation, it is necessary to slow down the dissolution process.

As shown in **Fig. S3**, for the same voltage and concentration of the NaOH solution, the deformability and the reversibility are different when cooperating with different volumes of the gallium droplet: the surface of the 0.1 mL deformed metal is obviously coated with a thick oxide skin, which significantly restricts the deformability (**Fig. S3-A**). In contrast to the 0.1 mL gallium droplet, the formation of the oxide layer on the surface of 0.3 mL liquid metal is obviously observed only in the narrow region close to the cathode (**Fig. S3-B**). Across the whole liquid metal with 0.5 mL, no obvious oxide gallium is visible, and the performance of the deformation is not completely digged up (**Fig. S3-C**). As previously mentioned, the rate of the reconfiguration depends on the net accumulation of the oxide gallium, and thus it is imaginable that the rate is decreased along with the increase of the gallium volumes (**Fig. S3**).





**Supplementary Figure S4 | Sequential snapshots for reversible deformation of liquid metal upon different volumes of gallium droplet.** The applied voltage and electrode spacing are 22 V and 6 cm, respectively. The concentration of the NaOH solution is 0.5 mol/L. **(A)** The volume of the gallium droplet is 0.1 mL. **(B)** The volume of the gallium droplet is 0.3 mL. **(C)** The volume of the gallium droplet is 0.5 mL.

## References

1. Tang, S. Y., et al. Liquid metal enabled pump. Proc Natl Acad Sci USA 111, 3304-3309 (2014).
2. Liu, T. Y., Sen, P., & Kim, C. J. Characterization of nontoxic liquid-metal alloy Galinstan for applications in microdevices. J Microelectromech S. 21, 443-450 (2012).
3. Morley, N. B., Burris, J., Cadwallader, L.C., & Nornberg, M. D. GaInSn usage in the research laboratory. Rev Sci Instrum. 79, 056107 (2008).

## Supplementary Movies

Supplementary movies (file attached/ available online)

### 1. Movie S1

- (1) Direct voltage: 10 V
- (2) Electrode spacing: 6 cm
- (3) Power-on time: 5 s
- (4) Gallium volume: 0.3 mL
- (5) Electrolyte solution: 0.5 mol/L NaOH solution
- (6) Electrodes: Platinum electrodes

### 2. Movie S2

- (1) Direct voltage: 20 V
- (2) Electrode spacing: 6 cm
- (3) Power-on time: 5 s
- (4) Gallium volume: 0.3 mL
- (5) Electrolyte solution: 0.5 mol/L NaOH solution
- (6) Electrodes: Platinum electrodes

### 3. Movie S3

- (1) Direct voltage: 30 V
- (2) Electrode spacing: 6 cm
- (3) Power-on time: 5 s
- (4) Gallium volume: 0.3 mL
- (5) Electrolyte solution: 0.5 mol/L NaOH solution
- (6) Electrodes: Platinum electrodes

### 4. Movie S4

- (1) Direct voltage: 30 V
- (2) Electrode spacing: 6 cm
- (3) Power-on time: 5 s
- (4) Gallium volume: 0.3 mL

(5) Electrolyte solution: 1 mol/L NaOH solution

(6) Electrodes: Platinum electrodes

## **5. Movie S5**

(1) Direct voltage: 15 V

(2) Electrode spacing: 6 cm

(3) Power-on time: 6 s

(4) Gallium volume: 0.4 mL

(5) Electrolyte solution: 1 mol/L Na<sub>2</sub>SO<sub>4</sub> solution

(6) Electrodes: Graphite electrodes

(7) After application of the external voltage, though the solution is initially neutral, when adding some phenolphthalein, the solution turns red while the deformed droplet does not reconfigure itself back into a sphere. When adding some 1 mol/L NaOH solution on the surface of the droplet, the deformed droplet contracts back into a sphere. Besides, after the application of external voltage, when adding some 7.2% HCl solution on the surface of the droplet, the deformed gallium changes its morphology and recovers back into a sphere. However, instead of the acidic or alkaline solution, the deionized water cannot make the deformed gallium change its shape reversibly.

## **6. Movie S6**

(1) Direct voltage: 30 V

(2) Electrode spacing: 6 cm

(3) Power-on time: 5 s

(4) Gallium volume: 0.5 mL

(5) Electrolyte solution: 0.5 mol/L NaOH solution

(6) Electrodes: Platinum electrodes

## **7. Movie S7**

(1) Periodic voltage: 10 V<sub>p-p</sub>, square-wave, 50% duty circle, 1 Hz frequency

(2) Electrode spacing: 3 cm

(3) Gallium volume: 0.3 mL

(4) Electrolyte solution: 0.5 mol/L NaOH solution

(5) Electrodes: Platinum electrodes

## **8. Movie S8**

- (1) Periodic voltage: 10 Vp-p, square-wave, 50% duty circle, 0.5 Hz frequency
- (2) Electrode spacing: 3 cm
- (3) Gallium volume: 0.3 mL
- (4) Electrolyte solution: 0.5 mol/L NaOH solution
- (5) Electrodes: Platinum electrodes

## **9. Movie S9**

- (1) Direct voltage: 8 V
- (2) Unfixed cathode or fixed cathode with 3 cm distance
- (4) Gallium volume: 0.5 mL
- (5) Electrolyte solution: 1 mol/L NaOH solution
- (6) Electrodes: graphite rod.